

The University of Chicago

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AND SYNTHESIS OF ORGANIC COMPOUNDS BY
ELECTRICAL DISCHARGES: ELECTRODE-
LESS AND GLOW DISCHARGES

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

By

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A Spectroscopic Study of the Decomposition and Synthesis of Organic Compounds by Electrical Discharges: Electrodeless and Glow Discharges

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In the chemical reactions which occur in electrical discharges through organic vapors and in the maintenance of the discharge, the simple ionization of the molecules, and the resultant formation of clusters, is found to be less important, and the breaking down into molecular, atomic and ionic fragments, more important than has heretofore been supposed. The fragments revealed by the spectroscope are CH, OH, NH, C₂, CN, N₂, CO, CO⁺, CS, S₂, H₂, C, C⁺, H, and S, and in addition H₂O and NH₃ are known to be formed. When the electrodeless discharge is in benzene vapor the pressure is rapidly lowered until the discharge is extinguished, but this effect is not found with the glow discharge. As compared with the electrodeless discharge, the spectrum from the glow discharge differs in the following respects: the C₂ bands are much less intense and only the fourth group of Swan bands appears appreciably. The line spectrum of C is less intense, and the prominent $\lambda 4267$ line of C⁺ disappears. The CH bands are very clear and that at $\lambda 3900$ is closer in intensity to that at $\lambda 4300$ than in the electrodeless discharge. The Balmer series of hydrogen is slightly more intense, and the many-line spectrum of H₂, not present with the electrodeless discharge, is prominent. In general the greatest intensity of the spectrum is given by the cathode glow and the edge of the negative glow near the cathode. The Crookes dark space is a region of very low intensity. The Balmer lines are of nearly uniform intensity throughout

except for a specially high intensity just at the cathode. The many line spectrum of hydrogen differs from the others in that it is scarcely visible in the cathode glow. With phenol many bands due to CO and CO⁺ dominate the spectrum of the glow discharge, though they are not found in the electrodeless discharge. In the electrodeless discharge the rate and nature of the reaction and the spectrum emitted are affected by the hydrogen to carbon ratio in such a way that the rate of reaction decreases as this ratio increases, and the fraction of gaseous products and the intensity of the spectra emitted by molecules which contain hydrogen increase with this ratio. Thiophene is decomposed into sulfur atoms (S), and molecules (S₂), and carbon monosulfide molecules (CS) in addition to molecules of carbon (C₂) and of monohydrocarbon (CH), atoms of hydrogen (H) and of carbon (C), and ions of carbon (C⁺) as had been shown before for the hydrocarbons. In the glow discharge both saturated and unsaturated hydrocarbons are decomposed at about the same rate to form the molecules and atoms listed above. The decomposition products from the glow unite to form brown or black solids somewhat similar to those formed in the electrodeless discharge. From the way in which the product is deposited and the intensity of the spectrum, the reaction is seen to be most rapid at the cathodeward edge of the negative glow.

I. INTRODUCTION

THE chemical changes which take place in electrical discharges through gases have been given a great deal of attention, but are not well known, especially when the gases consist of organic compounds. The present paper and an earlier one from this laboratory, indicate that the simple ionization of the molecules, and the resultant formation of clusters, plays a much less important role than has heretofore been supposed, and that the breaking down of the molecules into molecular, atomic, and ionic fragments, such as OH, CH, NH, C₂, CN, N₂, CO, CO⁺, H₂O, CS, S₂, C, C⁺, H, S, etc., is much more important in the determination of the products of the syntheses which occur and in the maintenance of the discharge, than has heretofore been supposed.

The chemical effects of electrical discharges through organic vapors have been studied by Lind and his co-workers,¹ Davis,² Austin and Black,³ Linder and Davis,⁴ Linder,⁵ Brewer,⁶ Kinoshita,⁷ Kohlschutter and Frumkin,⁸ and others.

¹ S. C. Lind and George Glockler, *J. Am. Chem. Soc.* **50**, 1767 (1928); **51**, 2811, 3655 (1929); S. C. Lind and D. C. Bardwell, *ibid.* **47**, 2675 (1925); **48**, 2335 (1926); S. C. Lind, D. C. Bardwell and J. H. Perry, *ibid.* **48**, 1556 (1926).

² A. P. Davis, *J. Phys. Chem.* **35**, 3330 (1931).

³ J. B. Austin and I. A. Black, *J. Am. Chem. Soc.* **52**, 4552 (1930).

⁴ E. G. Linder, *Phys. Rev.* **36**, 1375 (1930); Linder and Davis, *J. Phys. Chem.* **35**, 3649 (1931).

⁵ E. G. Linder, *Phys. Rev.* **38**, 679 (1931).

⁶ A. K. Brewer et al., *J. Phys. Chem.* **33**, 883 (1929); **34**, 153, 554, 1280, 2343 (1930); **35**, 1281, 1293 (1931).

⁷ S. Kinoshita, *Phys. Zeits.* **8**, 35 (1907).

⁸ V. Kohlschutter and A. Frumkin, *Rev.* **54B**, 587 (1921)

By the use of a mass-spectrograph Stewart and Olson⁹ found that hydrocarbons are broken up into shorter chain hydrocarbons by the impacts of the ionizing electrons. Eisenhut and Conrad-Ludwigshafen,¹⁰ also using a mass-spectrograph, obtained parabolas for particles of mass corresponding to C^+ , CH^+ , CH_2^+ , CH_3^+ , CH_4^+ , and similar fragments with larger numbers of carbon atoms.

In the work reported in the previous paper,¹¹ benzene and other vapors at pressures of approximately 0.1 mm were subjected to the electrodeless discharge, and decomposed with radiation of brilliant light, to form a resinous deposit on the walls of the discharge flask. A spectrographic analysis of the radiation showed that hydrogen atoms (H), carbon atoms (C), carbon ions (C^+), carbon molecules (C_2), and monohydrocarbon molecules (CH) were present. When oxygen was present in the vapor, molecules of hydroxyl (OH) and carbon monoxide (CO) were found in addition to those above; when nitrogen was present the spectrum also showed molecules of cyanogen (CN) and nitrogen (N_2), singly charged nitrogen ions (N_2^+), and imine molecules (NH).

In the work reported at present a few additional substances were studied in the electrodeless discharge. Some hydrocarbons with a higher ratio of H/C were used in a vain attempt to find any spectrum that might be attributed to dihydrocarbon molecules (CH_2). A sulfur compound, thiophene, gave the spectrum of sulfur atoms (S), sulfur molecules (S_2), and carbon monosulfide (CS) in addition to that shown by benzene.

It was hoped that critical potentials for the disintegration of hydrocarbons and the appearance of the spectra found could be determined by applying various accelerating voltages to the anode of a hot cathode tube filled with a hydrocarbon at low pressure. A visible glow was found to appear at potentials slightly below twenty volts in such a tube filled with benzene vapor, but it was not possible to obtain a glow of sufficient intensity and constancy to make a satisfac-

tory spectrographic analysis, so the method has been abandoned for the present.

A spectrographic analysis of the reactions of hydrocarbons in the glow discharge was considered valuable because the electrical phenomena are better understood than for the electrodeless discharge, and because so much work has been done on the products from such discharges. In the glow discharge as used in this work, without rapid pumping through the discharge, the product is mainly a yellow to black solid wall deposit. Both saturated and unsaturated compounds operated successfully.

The spectrum for hydrocarbons is similar to that for benzene in the electrodeless discharge, except that the spectrum of molecular carbon (C_2) is relatively less intense, and that of ionized carbon (C^+) does not appear at all. The spectrum of hydrogen molecules (H_2) appears, although it does not appear in the electrodeless discharge. For compounds which contain oxygen the spectrum of carbon monoxide (CO) is much more prominent than in the case of the electrodeless discharge.

The intensity of the emitted light was not found to be great enough to prove that all the molecules decomposed are broken up into the particles shown on the spectrogram. However, this is no proof to the contrary, since a part of the radiation from the tube is not in the frequency range studied, and since much of the radiation emitted is absorbed by the gas in the discharge.

II. APPARATUS AND PROCEDURE

a. Electrodeless discharge

The apparatus used in these experiments is shown in Fig. 1. Here F is a 1-liter Pyrex flask which contains the vapor studied. Over the mouth of the flask, a quartz window, Q , is attached with De Khotinsky cement. The tube E , sealed to the neck of the flask, acts as a trap for any solid product which may be thrown against the window, and, when necessary, as a liquid air trap. Around the flask in the plane passing through the window, is tightly wound a vertical coil of six turns of insulated, heavy copper wire. In addition to this coil, the high-frequency circuit consists of a 1 k.v.a. Thordarson transformer, V , which supplies 25,000 volts maximum, a spark

⁹ H. R. Stewart and A. Olson, J. Am. Chem. Soc. **53**, 1236 (1931).

¹⁰ H. O. Eisenhut and R. Conrad-Ludwigshafen, Zeits. f. Electrochem. **36**, 654 (1930).

¹¹ W. D. Harkins and D. M. Gans, J. Am. Chem. Soc. **52**, 5165 (1930).

gap, *S*, capable of adjustment by a screw and made of cylindrical zinc electrodes 1.7 cm in diameter, and a 0.00025 microfarad condenser, *C*. The frequency of the circuit, as determined by a radio receiver, was about 800 kilocycles per second.

An *n*-dibutyl phthalate vapor pump, *P*, which is backed by a Cenco Hyvac pump, is used instead of the mercury vapor pump used in the previous

changes, so that the stopcock *K* must be adjusted very carefully. The discharge causes a considerable evolution of heat, which is dissipated with a fan.

In the case of methane the apparatus is slightly modified, so that the vapor from the methane, which is condensed in a bulb immersed in liquid air, is led into the flask, *F*, through a side arm, and continuous pumping through the stopcock *J* is maintained.

The light which passes out through the quartz window, *Q*, is focused on the slit of a spectrograph. In this work a Hilger E 1 quartz spectrograph and a Steinheil GH glass spectrograph were used. A small plane silver mirror, placed when desired at an angle of 45° just in front of the quartz window, throws the spectrum of an iron arc on each plate, for comparison. For the work in the visible region, panchromatic plates were used. The deposit of a firmly adhering film of product necessitated a change of the window after each exposure, which lasted from one-half to several hours.

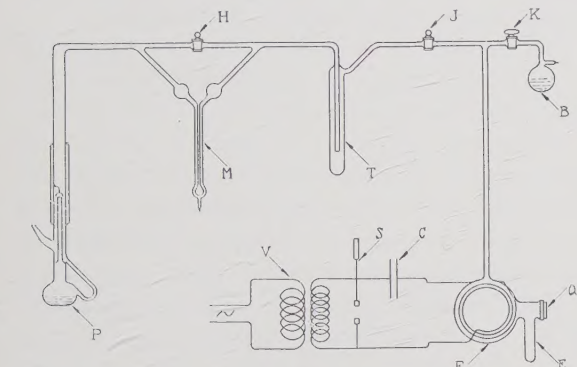


FIG. 1. The experimental arrangement for experiments with the electrodeless discharge.

work, so that all mercury might be kept out of the apparatus. Pressures are read by means of the manometer, *M*, which is filled with the *n*-dibutyl phthalate liquid. The differences in level are read against a millimeter scale with a magnifying lens. They can be read accurately to less than a millimeter of the liquid used, which is equivalent to 0.073 mm of mercury. By closing stopcock *H* the difference in pressure between the line side and the pump side is registered, the pressure on the pump side being taken as zero for the purposes of these experiments. The trap, *T*, can be used to keep the *n*-dibutyl phthalate vapor out of the flask and to keep the reacting substance out of the pumps.

The compound to be studied, properly purified and dried, is distilled under reduced pressure into the bulb, *B*, which is then sealed except for the outlet through stopcock *K*. The apparatus is then completely evacuated, the stopcock *J* is now closed, and kept closed permanently except during pressure measurements. The electrodeless discharge is now started, and the vapor admitted through *K* to the flask, where it is decomposed to form the solid product with the emission of light. The discharge is very sensitive to pressure

b. Glow discharge

The vacuum line used in these experiments is the same as that shown in Fig. 1, the discharge tube and electrical circuit are shown in Fig. 2.

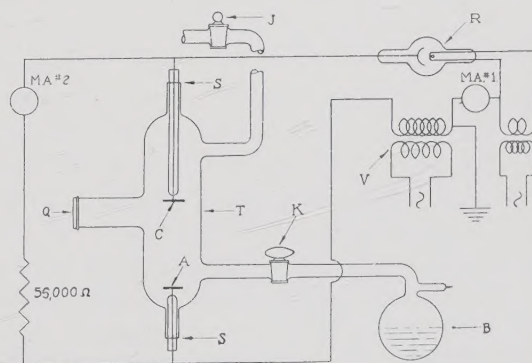


FIG. 2. The experimental arrangement for experiments with the glow discharge.

The discharge tube, *T*, is equipped with both inlet and outlet tubes, so that vapor may be pumped continuously through the discharge. The quartz window, *Q*, is sealed on to the side arm with wax. The electrodes *C*, cathode, and *A*, anode, are aluminum disks 2 cm in diameter and 1.5 mm thick, which are clamped to tungsten

leads sealed into glass tubes. These tubes fit into tubes at the ends of tube *T*, so that the electrode position may be adjusted at will. When the electrodes are in the desired position, vacuum tight seals are made at the joints, *S*, with picein wax. An electrode spacing of about 8 cm is used, the cathode being placed so that light from the cathode glow and negative glow come directly through the window.

In addition to the electrodes the electrical circuit consists of the 25,000 volt maximum, 1 k.v. a. transformer, the output of which is rectified by a single kenetron, *R*. The current flow is measured with a Weston d.c. milliammeter, No. 1, on the assumption that the reading represents the average for the half cycle in which current flows. The milliammeter No. 2 and 56,000-ohm resistance are shunted across the electrodes to measure the voltage drop. This was done in only one special experiment.

After evacuation of the system, the vapor is admitted to the tube, *T*, through stopcock *K* to a pressure of about 2 millimeters of mercury. The glow discharge is then started with a potential difference of 500 to 1,000 volts between the electrodes, and the vapor decomposes to form the solid product. A blue or green light is emitted in the familiar regions cathode glow, negative dark space, and negative glow. The positive column usually does not appear under the conditions of electrode spacing and pressure used, at higher pressures a striated positive column appears. The discharge is of the abnormal type, i.e., the current passed, which registers as 35 to 40 milliamperes, is greater than that required to make the glow completely cover the surface of the cathode. The discharge is accompanied by a considerable heating of the walls of the tube, and a fan is used for cooling.

The discharge is not particularly sensitive to pressure changes, but a pressure of about 2 millimeters which gave a dark space width of 1.5 or 2 millimeters was used throughout the work. With the saturates a continuous pumping through *J* is required in order to allow fresh vapor to flow into the discharge; with the unsaturates pumping is not required.

The tube is mounted vertically and the light which comes through the window is focused on

the slits of the spectrographs mentioned above, in such a way that the images of the cathode glow, negative dark space, and negative glow fall in different positions on the slit. This facilitates a comparison of the different regions of the discharge on one spectrogram. Panchromatic plates were not used in this work because they are rather slow, and several hours of exposure were required at best. The line $H\alpha$ is all that is lost in this way. Exposures of four or five hours were required; the window was cleaned between exposures.

The intensity of the light radiation is measured by means of a Kipp thermopile and Weston galvanometer, which were calibrated with a Bureau of Standards standard radiator. A quartz cell filled with distilled water is placed in front of the thermopile to filter out infrared radiation. The discharge is carried out in a quartz flask instead of the tube described above. Readings are taken at various points around the flask, before much deposit forms on the walls, then the total radiation is calculated by integrating over the whole surface.

III. PURIFICATION OF COMPOUNDS

The compounds studied in the electrodeless discharge were xylene, mesitylene, methane, pyridine, benzaldehyde, and thiophene. The methane was prepared by heating a mixture of sodium acetate and barium oxide, the gas being collected over water. The gas was then passed through a trap surrounded by solid carbon dioxide, bubbled through concentrated sulfuric acid, passed over phosphorus pentoxide, and condensed in a trap, connected as bulb *B*, which was surrounded by liquid air. With the other compounds, the purest reagents available were dried over sodium, barium oxide, phosphorus pentoxide, or anhydrous sodium sulfate, and a middle fraction distilled into the bulb *B* under reduced pressure.

The compounds studied in the glow discharge were benzene, n-heptane, methane, pyridine, and phenol. The purification or preparation was as above except in the case of methane. The methane was prepared in small quantities by heating the reagents mentioned above, in the closed evacuated system, the gas being immediately condensed in a trap surrounded by liquid nitro-

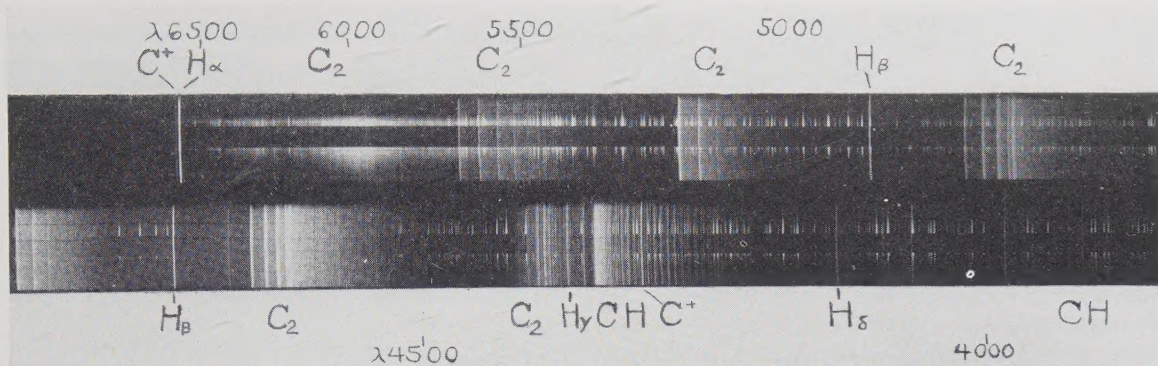


FIG. 3. Spectrum from the decomposition of benzene in the electrodeless discharge (by Gans). It was taken on the Steinheil spectrograph and shows the spectrum of the Fe arc for comparison.

gen. The gas was then dried and purified by repeated distillation over phosphorus pentoxide from one trap to another.

IV. EFFECTS OF THE ELECTRICAL DISCHARGES

a. Electrodeless discharge

(1) *Benzene, xylene, mesitylene and methane.* (Fig. 3.) The hydrogen to carbon ratios of these substances are, respectively, 1.00, 1.25, 1.33, and 4.00. Consequently there should be a definite trend of characteristics in the reaction as the vapor is changed from benzene¹² to xylene and mesitylene and to methane. In the case of benzene several thousand liters of the vapor were admitted to the discharge flask in the course of a half hour and decomposed to form a solid product. No cooling agent was required around the trap *E*, and not only did the pressure remain constant during the decomposition, showing no accumulation of permanent gas, but if at any time the inflow of fresh vapor was stopped, the pressure was reduced by the discharge to the point of extinction.

In the cases of both xylene and mesitylene the discharge ran continuously for long periods without the accumulation of enough permanent gas to stop the discharge. However, in contrast to the benzene, the discharge did not reduce the pressure sufficiently to extinguish itself when the inflow of either of these substances was stopped. Thus the condensation is less complete than that with benzene. The differences between xylene and mesitylene are not great enough to be ob-

served in the reaction, but the rate of formation of product was slightly less for mesitylene than for xylene, which in turn was less than that for benzene (1.2 grams per hour). The products from both substances are light brown in color and consist mainly of a loose powdery material, with some scaly material which clings to the walls of the flask.

The initial discharge is a greenish-white ring which turns into a white glow. The glow completely fills the flask at lower pressures, but has a non-luminous core at higher pressures. When the discharge is allowed to run without the inflow of fresh vapor the glow becomes very red, which shows that the spectrum of the α -line of the Balmer series of hydrogen has been greatly enhanced.

These data are summarized for all of the substances in Table I. The first column gives the color of the initial ring discharge, the second that of the glow. The third column gives the maximum pressure at which the discharge will operate when a spark gap of approximately 1.5 centimeters is used in the electrical circuit. This length and these pressures are somewhat greater than those actually used in the continuous runs. Column 4 states the color of the product, column 6 the physical form of the product, and the last column gives the approximate rate of formation of the solid product in grams per hour at the intermediate pressures used in the continuous runs.

With methane the pressure was found to rise slightly when the discharge was run through fresh vapor with both inlet and outlet from the flask closed. It was impossible to run the discharge with a continuous inflow of the methane

¹² Reaction of benzene described in the previous paper. (Reference 11).

TABLE I.

Substance	Color of discharge Ring	Glow	Max. press. 1.5 cm gap	Color of product	Form of product	Rate of forma- tion of product, g per hour
Xylene.....	Greenish-white	White to red	0.26 mm	Light brown	Powder and scales	1.0
Mesitylene.....	Greenish-white	White to red	0.30	Light brown	Powder and scales	0.8
Methane.....	Greenish-white	White to red	1.01	Light brown	Scales	0.0
Pyridine.....	Greenish-blue	Bluish-white to brown	0.28	Dark brown	Powder and scales	1.8
Benzaldehyde....	Greenish-blue	Blue and red to red	0.37	Dark brown	Powder and scales	1.2
Thiophene.....	Intense green	Purple to red	0.19	Dark brown to black	Some powder and heavy scales	0.7

unless the gaseous products were continuously pumped out. This is the kind of pressure effect that might easily have been predicted by observing the hydrogen to carbon ratio. Thus, the greater the value of H/C, the less complete is the condensation to a solid of very low-vapor pressure.

The photographs of the decomposition spectra of all three hydrocarbons are very much like those published for benzene in the previous paper. All five groups of the Swan bands are prominent, and the other groups of C_2 bands from $\lambda 4102$ to $\lambda 3998$ are present. The CH bands at $\lambda 4300$ and $\lambda 3900$ are both prominent, and the first five lines of the Balmer series of hydrogen are very strong. The line spectrum of C^+ and the line from the arc spectrum of C at $\lambda 2478$ were also observed to be

strong. The relative intensities for these and the other substances are tabulated in Table II. The figures are only approximate, and do not hold for a comparison between substances. The very long exposures gave a much greater blackening of the plate than is indicated by the table. The times of exposure given are for the visible and near ultra-violet position on the Hilger instrument. Except in the case of unusually long exposures in this position, the exposures in the second position, $\lambda 3200$ to $\lambda 2400$, were about twice as long.

As was expected, the intensities of the spectra of H and CH become greater as the value of H/C is increased. However, even with long exposures, no new bands appeared, and it must be concluded that if any CH_2 molecules are present, they are present in such small concentrations that their radiation in the region investigated is negligible in comparison with the radiation identified.

(2) *Pyridine*. The decomposition of pyridine, in contradistinction to the aniline described in the previous paper, went on continuously without the necessity of using a cooling agent on the side tube *E*. The difference between the behavior of aniline and pyridine must depend in part on the hydrogen to carbon ratios which are 1.17 and 1.00, respectively. Of course, the presence of the nitrogen atom is an additional factor which influences the behavior of both substances. The product from pyridine had a strong odor of bivalent carbon compounds, but did not give the positive litmus test for ammonia, which was found with aniline.

In addition to the spectrum shown by the hydrocarbons, the spectrogram showed the violet cyanogen bands from group II at $\lambda 4532$ to group V at $\lambda 3590$ very prominently. The β bands of NH at $\lambda 3360$ and $\lambda 3370$, the second-positive group of

TABLE II. *Relative intensities.*

Exposure, hrs.	Substance					
	Xy- lene 0.5	Mesity- lene 5.5	Meth- ane 3	Pyri- dine 1	Benzal- dehyde 1	Thio- phene 1
Intermediate decomposition product						
CH.....	4	4-5	3-4	3	3	3
Swan C_2 ...	4	4-5	2	3	3	3
All other C_2 .	2	3	1	1	0-1	0-1
$C^+(C)$	3	2-3	4	3	4	3-4
H.....	4-5	4-5	5	4	4	4
CN.....				5		
NH.....				3		
N_2				2		
N_2^+				2		
CO.....					1	
OH.....					2	
S.....						4
S_2						3
CS.....						5

Key: 1, Very weak; 2, weak; 3, average; 4, intense; 5, very intense.

N_2 at $\lambda 3577$, $\lambda 3371$, and $\lambda 3159$, and the first-negative group of N_2^+ at $\lambda 3914$ were also found to be present. Thus the spectrum is like that due to the aniline decomposition except that the bands due to C_2 and CH are relatively a little less intense.

(3) *Benzaldehyde*. The ratio of hydrogen to carbon is 0.86 for benzaldehyde, whereas, it is 1.00 for phenol. It is not surprising that the decomposition of benzaldehyde will run continuously without the use of a cooling agent on E , although liquid air was required to condense out the water vapor formed in the decomposition of phenol described in the previous paper.

The spectrum is similar to that for phenol except that the CO bands at $\lambda 2974$ and $\lambda 2832$ are relatively a little stronger and the OH band at $\lambda 3064$ a little weaker. The rest of the spectrum is similar to that from the hydrocarbons.

(4) *Thiophene*. Continuous decomposition was easily maintained as, for example, in the case of benzene. The product had a very dark color with a sort of metallic lustre, and most of it clung tenaciously to the walls of the flask. The color effects in the discharge were very beautiful, since there was much purple and red in the glow.

In addition to the spectrum shown by the hydrocarbons the spectrogram showed the line spectrum of S very prominently, and the band spectrum of S_2 . A very striking set of bands extending from about $\lambda 2850$ to $\lambda 2460$ was found. They are due to CS , and the appearance of the plate was much like that of one published by Martin.¹³ The bands were later analyzed and discussed more fully by Jevons.¹⁴

b. Glow discharge

(1) *Benzene*. (Fig. 5.) The discharge ran continuously without pumping out any gaseous products or using condensing traps, and at the pressures used the pressure was found to decrease somewhat when the discharge was passed without the inflow of fresh vapor. However, the effect of the reaction differed from that found in the electrodeless discharge in the fact that the discharge would not reduce the pressure to the point of extinction. The product formed at first in a

dark brown band on the walls of the tube in the region of the cathode. This film spread all over the tube, being lighter in color behind the electrodes. Later black spots appeared in it, and at the end of a number of hours of continuous running a considerable amount of gray black material, much like asphalt in appearance, was found in the tube, the original brown and yellow film being confined to a thin layer on the wall. None of the product was found loose as in the electrodeless discharge, though most of it could be scraped off the wall easily, but some clung very tightly. An analysis of the product gave $(C_{1.00}H_{0.89})_n$ as its average composition. The loss of one-tenth part of hydrogen is surprising, but was probably due to occasional pumping out through J to reduce the pressure, necessitated by improper regulation of the inlet K .

The solid product was formed at a rate of approximately 0.5 gram per hour, which is equivalent to the conversion of 0.00645 mole of benzene into a solid of the composition given above in the course of an hour. Since by the assumption used in measuring the current, the current was passed at a rate of 17.5 milliamperes, registering as 35, or 0.000655 equivalents of current per hour, there were 9.87 moles of benzene decomposed for every equivalent of current passed.

In measuring the intensity of the light radiation there was found to be a great deal of infrared radiation from the hot walls of the flask, and possibly some from vibration-rotation bands. This was successfully filtered out with a quartz cell filled with distilled water, which was found to give very good transmission in the blue region, where most of the light radiation lies. The values found are only approximate because the deflection was only a few millimeters on the scale of the galvanometer used, and because the fraction of transmission by the walls of the discharge flask and the filter was not known. From the spectrograms taken the average wave-length of the radiation was estimated to be 4200 angstroms. The total radiation in the region measured was found to be at the rate of 4.98×10^{-3} watt, which is equivalent to 1.07×10^{16} quanta per second. This means that there were approximately 102 molecules of benzene decomposed for each quantum of energy radiated through the quartz in this region.

¹³ W. B. Martin, Proc. Roy. Soc. **A89**, 121 (1913); plate 6, No. 4.

¹⁴ W. Jevons, Proc. Roy. Soc. **A117**, 351 (1927).

TABLE III.

Substance	Color of discharge	Color of product	Form of product	P.D. in volts	Rate of formation of product (g per hr.)	Moles per equiv. of current	Molecule per quantum of radiation
Benzene ..	Blue-green to white	Black to yellow	Powder and gum	800	0.5	9.87	102
n-heptane..	Blue-green to pink	Black to brown	Powder	800	0.15	2.47	25.5*
Methane..	Blue-green to pink	Black to brown	Powder	450 to 650	0.03	3.28	38.2*
Pyridine..	Blue to violet	Black to brown	Powder and scales	800	0.14	2.75	
Phenol...	Blue-green	Black to brown	Powder and scales	650	0.16	2.40	

* Estimated assuming radiation equal to that from benzene decomposition.

These data are summarized in Table III. The first column gives the color of the discharge, the second the color of the product, and the third the physical form of the products from the different substances. Column four gives an approximate value of the potential difference across the discharge, which was estimated by a comparison of the observed average value of the current with a curve for current against voltage. This curve had been obtained by varying the pressure during an experiment in which the voltage and current were both measured. Column five presents the rate of formation of solid product in grams per hour, column six the rate of conversion of the original vapor to solid in moles per equivalent of current passed, and the last column shows the

rate of conversion in terms of molecules per quantum radiated through the quartz.

The spectrum obtained was generally similar to that of benzene and other hydrocarbons in the electrodeless discharge, but there are a number of noteworthy differences. The C_2 bands are much less intense and only the fourth group of the Swan bands appears appreciably. The line spectrum of C is less intense, and the $\lambda 4267$ line of C^+ , which is very prominent in the electrodeless discharge, does not appear at all. The CH bands are very clear, that at $\lambda 3900$ possibly being closer in intensity to that at $\lambda 4300$ than in the electrodeless discharge. The Balmer series of hydrogen appears to be a little more intense, and the many line spectrum of H_2 , which was not found at all in

TABLE IV. *Relative intensities for glow and electrodeless discharges.*

	Substance									
	Benzene		n-heptane		Methane		Pyridine		Phenol	
	<i>G</i>	<i>E</i> *	<i>G</i>	<i>E</i> *	<i>G</i>	<i>E</i>	<i>G</i>	<i>E</i>	<i>G</i>	<i>E</i> *
Exposure, hrs.....	4	0.5	5	0.5	3.5†	3	4	1	2†	1.5
Intermediate decompos. product										
CH.....	4	4	4	2	4	3	3	3	2	3
Swan C_2	3	5	3	0	0	2	1	3	2	3
All other C_2	2	2	2	0	0	1	0	1	0	2
C.....	1	3	1	1	?	3	3	3	4	3-4
C^+	0	3	0	1	0	0	0	3	4	3-4
H_2	5	4	5	5	5	5	4	4	4	3
H_2	3	0	4	0	4-5	0	1	0	1	0
CO.....									4-5	1
CO^+									4-5	0
OH.....									3	3
CN.....							5	5		
N_2^+							4	2		
N_2							0	2		
NH.....							3	3		

Key: 1, Very weak; 2, weak; 3, average; 4, intense; 5, very intense.

* Data taken from previous paper (reference 11). Heptane is not a fair comparison because there was no pumping out in the electrodeless experiment.

† Time is for Steinheil instrument, others are for Hilger.

the electrodeless discharge, is very clear in the spectrum of the glow. The relative intensities are summarized in Table IV, where they are compared with those in the electrodeless discharge.

The spectrum indicates the existence of the intermediate decomposition products C and H atoms, C_2 , CH, and H_2 molecules in the glow discharge through benzene vapor.

The variations in intensity, as one looks up and down the spectrum lines across the different parts of the discharge, are of interest. Most parts of the spectrum vary in the same manner, the most intense regions are the cathode glow and the edge of the negative glow toward the cathode, the Crookes dark space is a region of very low inten-

sity, and there is some fading out as one goes from the edge out into the negative glow. The Balmer lines show fairly uniform intensity throughout except for a very intense and blurred tuft just at the cathode. The many line spectrum of hydrogen differs from the rest in that it is scarcely visible in the cathode glow, and grows more intense as one progresses into the negative glow. A spectrogram taken of the region considerably farther out into the negative glow was similar to that portion of the negative glow a few millimeters from the edge except for a general decrease in intensity. The above data are summarized for all of the substances in Table V, where a comparison of intensities is made for the regions of the cathode glow,

TABLE V. *Relative intensities in different parts of the discharge.*

Intermediate decomposition product	Substance														
	Benzene			n-heptane			Methane			Pyridine			Phenol		
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
CH.....	4	3-4	3	4	3-4	3	4-5	4	4	3	2	1	2	1	0-1
Swan C_2	3	3	2	3	3	2	0	0	0	1	1	0-1	2	1	0
All other C_2	1	2	1	2	2	1	0	0	0	0	0	0	0	0	0
C.....	1	1	0	1	1	0	?	?	?	3	3	2	5	4	3
C^+	0	0	0	0	0	0	0	0	0	0	0	0	4	4	4
H.....	5	5	5	5	4	4	5	4-5	4-5	4	4	3	4-5	4	4
H_2	0-1	3	3	1	4	4	4-5	4-5	4-5	0-1	1	1	1	1	1
CO.....													5	4	3
CO^+													4	4	4
OH.....													3	2	1
CN.....										5	5	5			
N_2^+										3	3	4			
NH.....										3	3	3			

Key: a, Cathode glow; b, edge of negative glow; c, negative glow about 5 mm from edge. 1, Very weak; 2, weak; 3, average; 4, intense; 5, very intense.

the edge of the negative glow, and that portion of the negative glow a few millimeters from the edge.

(2) *n-heptane*. As would be expected, there was found to be a large quantity of gaseous product formed in the decomposition of heptane, which was shown by a large increase in pressure when the discharge was run through fresh vapor with both inlet and outlet closed. Constant pumping out was employed in the continuous runs, and a solid product very much like that from the benzene in appearance was obtained. Analysis showed that the hydrogen content of the product is slightly greater, the average composition being $(C_{1.00}H_{1.13})_n$.

The spectrum was found to be similar to that from the benzene except for a small increase in

the intensity of the many line spectrum of hydrogen.

(3) *Methane*. (Fig. 5.) Although the percentage of gaseous product must be greater in this case than for the heptane, the pressure increase in the closed system was much less noticeable on account of the smallness of its molecules. The rate of formation of product was very slow, a brown film, with some black on the interior, was formed. The average composition of the solid was found by analysis to be $(C_{1.00}H_{1.25})_n$. The analyses of the products from benzene, heptane, and methane show that the composition of the product is directly influenced by the hydrogen to carbon ratio of the reacting substance.

The spectrum is interesting in that the C_2

bands disappeared altogether, and the spectrum of H_2 became very strong.

(4) *Pyridine*. The characteristics of the operation were very much like those for benzene, except that the discharge had a great tendency to

jump back to the glass tube holding the cathode as soon as some product had formed on this tube. This heated the glass so much that small holes developed, and a great deal of trouble was experienced in keeping the apparatus vacuum tight.

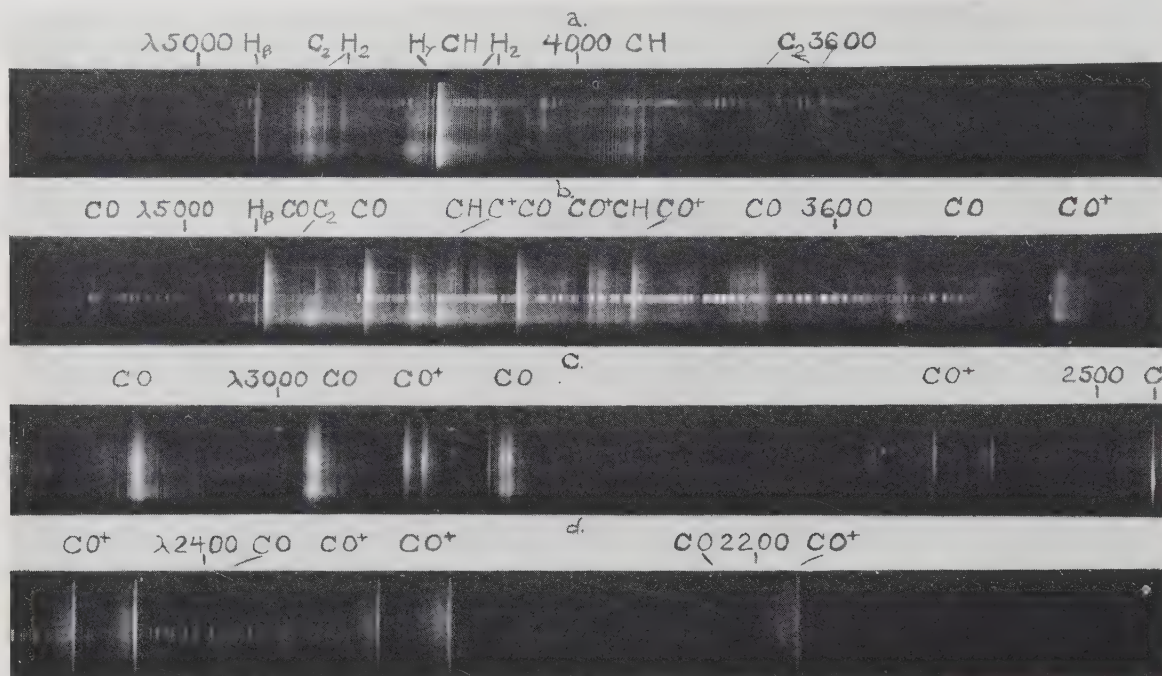


FIG. 4a. Spectrum from the decomposition of benzene in the glow discharge, as taken by the Hilger spectrograph, using the iron arc for comparison. b, c, d. Spectra from the decomposition of phenol in the glow discharge. Hilger spectrograph.

The product was more scale-like in character and clung tightly to the glass walls. It had a strong odor of bivalent carbon compounds.

The spectrum differed from that in the electrodeless discharge in the decrease in intensity of the spectrum of C_2 , the disappearance of that of C^+ , and the presence of a spectrum due to H_2 . The first negative group of N_2^+ shows at $\lambda 4278$ and $\lambda 4237$ in addition to the band at $\lambda 3914$, which was the only one showing in the electrodeless discharge. The cyanogen "tail" bands¹⁵ are quite prominent in the glow discharge, but very faint in the electrodeless discharge.

(5) *Phenol*. (Fig. 4.) The operation was not very satisfactory, since the vapor pressure of phenol at room temperature was lower than that needed for the best operation of the discharge.

However, sufficient decomposition and satisfactory operation for the spectrograph were obtained by the use of a heating bath around *B*. There appeared to be a slight rise in pressure when the discharge was run through the fresh vapor in the closed system. Constant pumping out was used to insure the inflow of fresh vapor. The product formed slowly, but had an appearance much like that from the hydrocarbons.

The spectrum differed from that of the other substances in the glow discharge by the appearance of the line due to C^+ at $\lambda 4267$, the relative decrease in intensity of the spectrum of H_2 , and the complete domination of all the region investigated by a great many bands due to CO and CO^+ , which had not been found in the electrodeless discharge. These bands are the angstrom bands of CO , the third and fourth positive groups of CO , the first negative group of CO^+ , the comet-

¹⁵ A. S. King, *Astrophys. J.* **14**, 323 (1901).

tail¹⁶ bands of CO^+ , and the Baldet-Johnson¹⁷ bands due to high pressure CO^+ . Bands at $\lambda 4830$, $\lambda 3895$, and $\lambda 3679$, which were first reported by Duffendack and Fox¹⁸ and thought to belong to the angstrom system, were quite prominent. There was a fairly prominent band at $\lambda 4664$, which was not identified in a fairly exhaustive search of the literature, but which was much like the angstrom bands in appearance.

V. DISCUSSION

In the electrodeless discharge there are two electrical fields, one an alternating electrical field, parallel to the axis of the solenoid, and the other an electromagnetic field whose electrical energy is in rings perpendicular to the axis of the solenoid. Both fields may play a part in the discharge reaction, but the electromagnetic field must be most important in the initial ring discharge, and electrostatic field parallel to the axis most important in the glow which comes later. The pulsating d.c. electrostatic field between the electrodes in the glow discharge is comparable to the field responsible for the glow in the electrodeless discharge.

The differences between the reactions in the two discharges, which are shown by differences in their spectra and products, must depend on the differences in pressure and electrical fields. For instance, it is conceivable that more collisions favorable for the combination of hydrogen atoms into molecules take place at the higher pressure in the glow discharge than in the electrodeless discharge, thus accounting for the appearance of the many line spectrum of hydrogen in the glow discharge. The Baldet-Johnson high-pressure bands of CO^+ may appear in the one rather than the other, not only because of the pressure difference, but also because of a possible difference in electron energy, since energies of the order of one hundred electron volts are required for the appearance of these bands.

¹⁶ A. de la Pluvinel and F. Baldet, *Astrophys. J.* **34**, 89 (1911).

¹⁷ Baldet, *Comptes Rendus* **178**, 1525 (1924); Johnson, *Proc. Roy. Soc.* **A108**, 343 (1925).

¹⁸ O. S. Duffendack and G. W. Fox, *Astrophys. J.* **65**, 214 (1927).

It is probable that the energy of electron impact is the most important factor in the smashing of the molecules of the original substance into the spectroscopically observed intermediates. There must be many positive ion impacts, but evidence points to the fact that they are quite ineffective until they acquire velocities comparable to the electron velocities required to produce dissociation or ionization,¹⁹ velocities which they almost certainly cannot acquire. Collisions of the second kind no doubt play an important part in the reaction. The fact that the rate of reaction is most rapid, and that one of the most intense portions of the spectrum is located at the edge of the

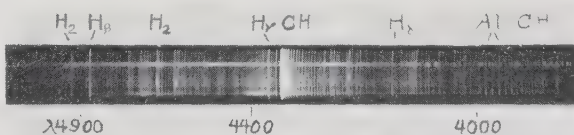


FIG. 5. Spectrum from the decomposition of methane in the glow discharge, with the iron arc reference spectrum taken on the Steinheil instrument.

negative glow, where the density of high velocity electrons is greatest, points to the importance of electron impacts in the reaction.

While there is no direct evidence that all of the molecules are smashed into the intermediates found, it seems probable that most of them are so decomposed, or at least that these active particles initiate the most of the reaction. Certainly the energy available, about 80 electron volts per molecule of benzene reacting and more for the other substances, should be sufficient for the breaking up of all the reacting molecules. The breaking up of a molecule may take place directly by electron impact, there may be ionization or excitation by electron impact followed by dissociation, or the ionization or excitation may be due to collisions of the second kind, or to radiant energy, and again be followed by dissociation.

In conclusion, it must be stated that the phenomena in reactions of this type are so complicated that it would be foolish to postulate any definite mechanism as being responsible for the reaction.

¹⁹ Compton and Langmuir, *Rev. Mod. Phys.* **2**, 123 (1930).

